ABSTRACT

Polymers, over the years, have found several industrial applications ranging from mundane (structural and house hold items, packaging materials, electrical insulation or paints) to futuristic (space, robotics, green energy technologies and biomaterials). Apart from the conventional use of polymers, the last three decades has witnessed emergent applications in novel and exciting fields. Some of the recent areas where these materials are rapidly gaining importance including conducting polymers for electronics and sensing, proton exchange membranes for fuel cell applications, electrolytes for solid-state devices, smart coatings, hydrogels and self-assembled aggregates for controlled drug release, wound-dressings and alternate bio-implants. Considering the immense prospects of polymer/polymer-nanocomposites, this thesis is an attempt to design and demonstrate the versatility of a model polymer matrix and its nanocomposites based on interpenetrating networks approach.

An interpenetrating polymer network (IPN) is a unique type of polymer blend and can be defined in general as a mixture of two or more polymer networks, one of which is being synthesized in the immediate vicinity of the other growing or already formed networks. The presence of cross-links and entanglements increases the miscibility of the component polymers compared to usual blends of them and leads to a material with good dimensional stability. Among several classes of IPNs, semi-IPNs are the combination of one cross-linked and one or more linear or branched polymers. Specific non-covalent interactions between the linear and the cross-linked component can lead to a semi-IPN system where the linear or branched polymer is definitely trapped in the structure although not covalently cross-linked. The aim of these types of polymer associations in general is to obtain materials with

(a) better mechanical properties, (b) dimensional stability and (c) a possibly improved combination of the properties of its components. IPNs and semi-IPNs have found several applications such as, hydrogels, smart coatings, etc.

In recent years composites of nanomaterials-both metal and metal oxide and organic polymers have attracted a great deal of attention due to their advantageous properties and many new characteristics compared with corresponding single-phase nanoparticles or polymers. These polymer-nanocomposites are considered to be novel functional materials with a wide range of potential applications like, biomedical applications, non-linear optics, mechanically reinforced light weight component, energy storage devices, etc.

In this thesis, a series of polymer- nanocomposites of polyurethane based semi-IPN, metal oxide and metal nanoparticles embedded polyurethane networks have been designed, synthesised and explored for three different applications. Keeping pace with the globally intensified research efforts in energy technologies; polymer-nanocomposites of polyurethane based semi-IPNs and titania have been investigated for their feasibility as solid polymer electrolytes (SPEs) as the primary focus of this thesis. In addition, metallic silver and palladium nanoparticles embedded in polyurethane networks with promising antibacterial properties and catalyst support matrix have been demonstrated respecively.

A general definition for a solid polymer electrolyte (SPE) is ‘a mixture of a salt in an ion-solvating polymer that configures a dry and solid electrolyte system with electrical conductivity values suitable for electrochemical devices’. The science of solid polymer electrolytes is a highly specialized interdisciplinary field, which encompasses the disciplines of polymer science, electrochemistry, organic and

inorganic chemistry. Literature survey evidently shows, during the past three decades it has been the research topic of numerous investigations by physicists, chemists and engineers in various avenues of applications envisaged.

The study of polymer electrolytes was first initiated by Wright et al in 1973. But their technological significance was not appreciated until the research undertaken by Armand et al in 1978. This group claimed that the complexes formed from the alkali metal salts and PEO were capable of demonstrating significant ionic conductivity and they highlighted their possible application as battery electrolytes. This work inspired intense research and development on the synthesis of polymer electrolytes, physical studies of their structure and charge transport, theoretical modeling of the charge transport processes and the physical and chemical properties of the electrode/electrolyte interface. The prerequisites for a polymer electrolyte to be used in rechargeable batteries are i) high ionic conductivity at ambient and sub-ambient temperatures, ii) good mechanical strength, iii) appreciable cationic transference number, iv) thermal and electrochemical stabilities, v) good compatibility with electrodes, etc.

Poly(ethylene oxide) (PEO) was the earliest and most extensively studied polymer host system. PEO shows low ionic conductivity, 10^{-7} S cm^{-1} to 10^{-8} S cm^{-1}, at ambient and sub-ambient temperature because of its considerably crystallinity below melting temperature, ~ 60 °C. Besides PEO, several polymers such as, poly(propylene oxide) (PPO), poly(phosphazene) (PPZ), poly(siloxane), poly(acrylonitrile) (PAN), polyvinylidene fluoride (PVDF), polyvinylidene fluoride-co-hexafluoro propylene (PVdF-co-HFP), etc. have been investigated as potential electrolytes and now scientists have come to an agreement that it is unlikely to

synthesize new polymers having significantly higher ionic conductivity. In this regard, structural modifications like, blending, grafting, co-polymerization and cross-linking of the existing polymers are the most viable alternatives to enhance their electrical properties. Among such modifications, formation of polymer networks is suggested to be the most effective strategy to achieve low degree of crystallinity as well as good mechanical stability. In this perspective, IPN and semi-IPN are special classes of polymer networks that can be tailored effectively to suit specific end uses.

Considerable progress has been achieved in recent years, in designing new polymer electrolytes based on organic-inorganic hybrids or nanocomposite systems. These solid polymer electrolytes combine the solvating power of the polymer matrix with the presence of inorganic networks, which provide higher chemical stability and better mechanical properties than pure organic polymers. The hybrid concept seems to be particularly well adapted for the production of advanced solid materials presenting ion-conducting properties, with the advantage of replacing viscous liquid systems with solid or rubbery materials.

Generally, electrically insulating, chemically and electrochemically inert, high surface area, sub-micrometer size particulate fillers such as TiO_2, ZrO_2, Al_2O_3, ZnO and hydrophobic fumed silica were incorporated into the polymer matrices to form nanocomposite polymer electrolytes or nanocomposite ceramic electrolytes. The nanocomposite-polymer electrolytes are multiphase, mostly two-phase solid systems.

Advantages of the nanocomposite-polymer electrolytes are many folds like, enhancement of ionic conductivity especially at low temperatures, decrease in the

path length for ion transport and improved stability at the interface with electrodes. Moreover, composite nanostructured materials designed to include shorter electronic conductive paths could decrease the inner resistance of lithium ion batteries, leading to higher specific capacities even at high charge/discharge current rates.

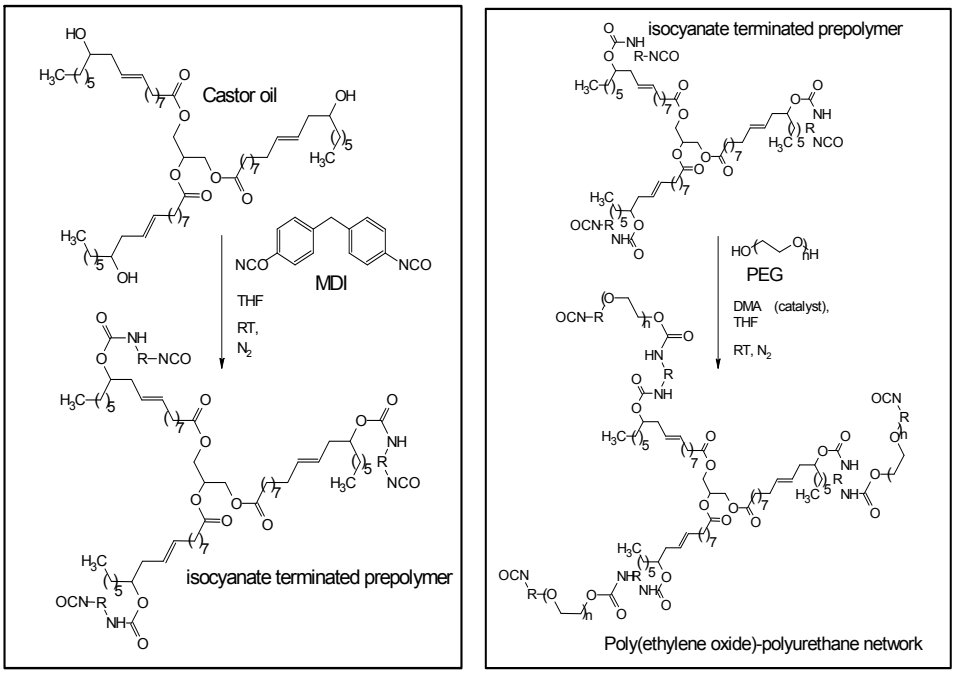
The work presented in this thesis is a sincere effort towards developing materials that combine the advantages of polymer networks with those of nanomaterials viz. an organic-inorganic hybrid. Two classes of semi-IPN: i) poly(ethylene glycol)-polyurethane/ polyacrylonitrile (PEG-PU/PAN) and ii) poly(ethylene glycol)-polyurethane/poly(ethylene glycol)diacrylate (PEG-PU/PEGDA) were chosen as the preferred host matrices. Synthesized bare titania (BT) and 4-*tert*-butylcatechol functionalized titania (CT) were the nanomaterials of choice to tailor the electrolyte morphology and properties. Furthermore, composites of polyurethane with metallic silver and palladium have been synthesized and applied as substrates for antibacterial activity and catalysis respectively.

The work carried out has been structured into five chapters:

Chapter 1 is an introduction to the science of solid polymer electrolytes. This chapter gives detailed information on the status and progress in the field of solid polymer electrolytes. Several polymers as host in polymer electrolytes, their advantages and disadvantages, different salts composed of different cations, anions and valence states have been discussed elaborately.

Chapter 2 discusses the synthesis of semi-interpenetrating polymer networks of poly(ethylene glycol)-polyurethane and poly(acrylonitrile) and their nanocomposites with bare titania as well as 4-*tert*-butylcatechol coated titania

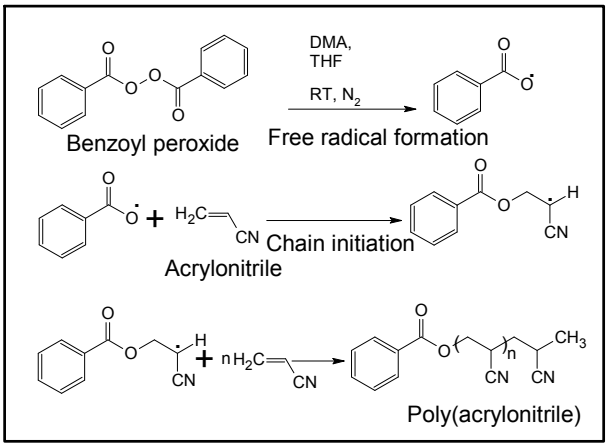
nanoparticles. These free standing semi-IPN-nanocomposite electrolyte films were characterized for their morphological and thermal properties. The effects of titania loading, nanoparticles surface functionalization, ion-polymer and polymer-nanoparticle interactions on morphology, thermal properties and ionic conductivity were evaluated in details.



Scheme 1. Reaction of castor oil and diphenylmethane diisocyanate to give an isocyanate-terminated prepolymer network in the first step of the reactions. In the next step the isocyanate-terminated prepolymer reacts with poly(ethylene glycol) to form poly(ethylene glycol)-polyurethane networks.

PEG-PU/PAN semi-IPN incorporated with lithium perchlorate salt were synthesized by two mutually exclusive polymerization processes where PEG-PU networks were formed by polycondensation reactions of castor oil (CO), diphenylmethane-4-4'-diisocyanate (MDI) and PEG, where as the second component, PAN was formed in the reaction medium simultaneously by free radical

polymerization of acrylonitrile. The efficiency of IPN formation was confirmed by determining THF (tetrahydrofuran) soluble fraction of the cured films. The average THF soluble fraction was found to be less than 5-7%, which indicates that the reaction proceeds with conversion > 95%.



Scheme 2. Reaction to show free radical polymerization of acrylonitrile to produce polyacrylonitrile by using benzoyl peroxide as free radical source.

All the semi-IPN and their nanocomposite films were characterized by FT-IR, XRD, TEM, TG-DTA and DSC. FT-IR confirmed the formation of the polyurethane networks. There are strong interactions between the polymer matrix with the surface of TiO_2 nanoparticles as well as between the Li^+ ions and the polymer as reflected by an enhanced red shift in the C-O-C stretching vibrations. XRD indicates significant change in the degree of crystallinity of PEG that occurs after the formation of PEG-PU/PAN semi-IPN. Incorporation of $LiClO_4$ in the semi-IPN reduces crystallinity further which indicates the formation of extensive cross-links between Li^+ ions and ether oxygen atoms of the polymer chains. TEM micrographs show that nanophase separated PAN (size ~ 50-400 nm) phases are well-dispersed throughout the PEG-PU networks. The even dispersion and low

nanoparticles agglomeration apparent from the micrographs also indicate a reasonable degree of polymer-nanoparticles interaction. Thermal stability of the semi-IPN and its titania nanocomposites were evaluated by thermogravimetry (TG).

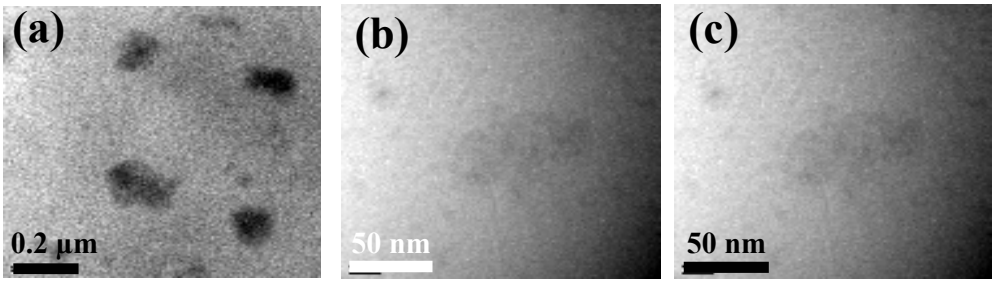


Figure 1. Transmission electron micrographs of synthesized semi-IPN titania nanocomposite films: **(a)** 5 wt% bare titania (P321-5BT). The 50-400 nm domains of poly(acrylonitrile) phase distributed in the poly(ethylene glycol)-polyurethane matrix are indicated; **(b)** Enlarged image of P321-5BT. The nanostructured titania particles, ~ 5-20 nm are also seen dispersed within the poly(ethylene glycol)-polyurethane matrix other than the larger PAN domains; **(c)** Enlarged image of 5 wt% surface modified titania nanocomposite film (P321-5CT) depicting the interspersed CT-particles in the semi-IPN matrix. The HRTEM images were collected on a JEOL TEM 2010 microscope at operating voltage 200 kV.

The TG-DTA traces indicate that the semi-IPN and semi-IPN-titania nanocomposites are thermally stable up to 230 °C. DSC analysis indicates PEG-PU and PAN form a well-mixed polymer matrix. After incorporation of $LiClO_4$ in the PEG-PU/PAN networks glass transition temperature (T_g) increases and melting temperature disappears which again indicates the formation of extensive cross-links by Li^+ ions with the ether oxygen atoms of PEG. DSC studies further demonstrated no substantial change in the thermal properties of the polymer-nanocomposite matrices even with increased amounts of TiO_2 loading (up to 5 wt%) and T_g (~ - 38 °C) remained well below the ambient temperature.

Chapter 3 describes the electrical behaviour of the synthesized semi-IPN and its nanocomposite materials by both direct current (dc) experimentation and alternating current (ac) impedance spectroscopy. The ion conduction and transport behaviour in the semi-IPN polymer-titania nancomposites were evaluated by dc conductivity studies. An enhancement in ionic conductivity for all the semi-IPN-nanocomposites was observed. It can be rationalized by considering that the polymer-nanoparticle complexation takes place in the near vicinity of the nanoparticle surface. The interfacial dynamics possibly creates smaller domains of PEG segments wherein the Li^+ ions are more loosely cross-linked under the circumstances of competitive interactions. Higher ionic transport within these domains contributes towards the overall increase in the bulk conductivity. A comparison of the conductivity behaviour between the nanocomposite systems consisting of bare titania and catechol-functionalized titania, the above rationale seems to hold good. Since polymer-nanoparticle surface interactions are expected to be more pronounced for the bare titania composites, the effect is reflected as an enhanced conductivity in P321-xBT matrices when compared to P321-xCT samples particularly at higher weight percent loading (here the digits stand for the ratio of wt% of PEG-PU, PAN and EO to Li ratio respectively whereas 'x' denotes wt% loading of BT or CT). From the Arrhenius plots it is evident that the ionic conductivity for all the semi-IPN-nanocomposites of functionalized titania levels off at higher temperatures and appears to be independent of the CT loading. Estimation of transference number indicates charge transport occurs predominantly by ions and the transport number is temperature dependent. The system P321-5BT showed maximum conductivity, 8.2×10^{-6} Scm^{-1} at 30 °C.

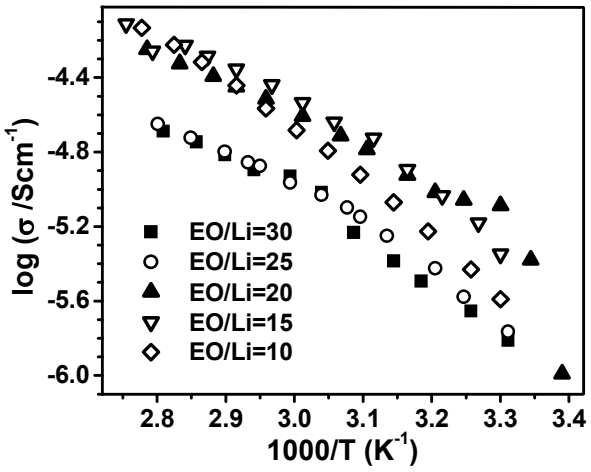


Figure 2. Plots of logσ vs 1000/T for the semi-IPN nanocomposite system P321-5BT with salt concentrations of EO/Li = 30, 25, 20, 15 and 10.

In the *ac*- impedance spectroscopy analysis an attempt has been intended to provide a detailed insight into the ion transport mechanisms at play in the synthesized semi-IPN- nanocomposite electrolytes. Spectroscopic plots of the real part of conductivity, $\sigma'(\omega)$ were fitted using the universal power law (UPL) equation. The UPL exponent, p was found to be in the range 0.26 to 0.87, which indicates that the initial site relaxation rate is always higher than the back hop rate and the ionic migration in these electrolytes is predominantly due to cationic hopping. Moreover, Debye relaxation times, τ_{peak} obtained from the Lorentzian fits are higher than the initial site relaxation time, τ_1 obtained from the UPL equation fits.

The results presented in this chapter clearly bring out the fact that the overall electrical behaviour of the investigated semi-IPN-nanocomposite polymer electrolytes depends on the temperature, type (i.e. bare or functionalized) and % loading of titania nanoparticles, ion-ion, ion-polymer and polymer-nanoparticles interactions together with polymer chain dynamics.

Summing up, the physico-chemical properties and Li^+ ion conductivity behaviour of this new class of polymer-nanocomposites holds promise for its potential use as SPEs.

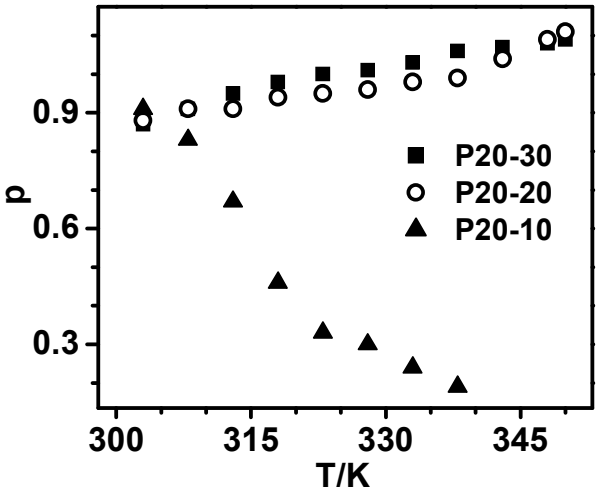


Figure 3. Plots of power law exponent, p against temperature.

Chapter 4 gives an insight into the synthesis and characterization of semi-IPN based on poly(ethylene glycol)-polyurethane/poly(ethylene glycol)diacrylate (PEG-PU/PEGDA) and its nanocomposites with both bare and 4-*tert*-butylcatechol modified titania. Salt doped semi-IPN were prepared by the addition of PEGDA and lithium perchlorate ($LiClO_4$) to a growing networks of PEG-PU. Formation of polyurethane was established by FT-IR through the appearance of C=O stretching frequency of urethane linkage at 1736 cm^{-1}. XRD shows PEG becomes amorphous after being cross-linked with PEGDA and DSC analysis proves that in the semi-IPN, PEGDA phase gets separated out when its concentration is 30 wt%. All the semi-IPN and nanocomposites are amorphous as no melting dips were observed in the DSC traces. TG-DTA traces indicate all the semi-IPN are thermally stable up to ~ 220 °C.

dc- Conductivity studies showed increment of electrical conductivity of the semi-IPN with increasing amount of PEGDA. It may be rationalized in the following manner. With increasing amount of PEGDA, T_g is decreasing, making the polymer chains more flexible, thereby facilitating ion transport. Moreover, added amount of PEGDA renders increased amount of host polymer available for $LiClO_4$ dissolution. So, the possibility of formation of contact ion pairs of the type $[M^+X^-]^0$ and triple ions of the types $[M_2X]^+$ and $[MX_2]^-$ (where M^+ and X^- are cation and anion of the salt MX) diminishes. Consequently effective concentration of free ions increases and so, ionic conductivity increases. Conductivity is decreasing with increasing salt concentration. It was explained by the fact that with increasing amounts of salt more number of contact ion pairs and triple ions are formed. So, the number of free ions decreased.

Secondly, with increasing amount of salt T_g increases, which makes the ion movement restricted. Both of these factors contribute to decrease electrical conductivity. Maximum conductivity attained was 3.0×10^{-6} Scm^{-1} at 30 °C for the system P30-30-2BT, where the numbers represent the amount of PEGDA in wt%, EO/Li ratio and loading of bare titania respectively. The power law exponent, p obtained from the fitting parameters of the profiles of the real part of ionic conductivity, $\sigma'(\omega)$ vs. log *f* was found to depend on polymer electrolyte composition and the investigation temperature. It varies in the range 0.40-1.20, which implies that depending on experimental temperature and electrolyte composition ionic migration occurs due to cationic hopping and after a certain temperature (~ melting temperature of PEG) anionic hopping results in the cation migration without any substantial geometrical site relaxation.

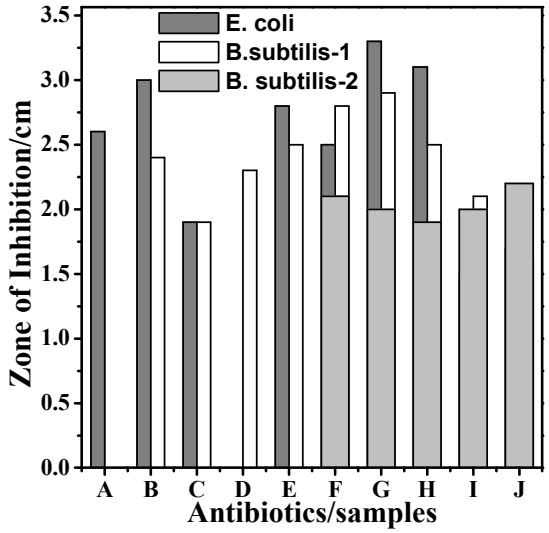


Figure 4. Comparison of antibacterial activity in terms of the zone of inhibition of the discs with standard antibiotics where A-E are antibiotics penicillin, tetracycline, ampicillin, kanamycin, and streptomycin respectively, and F-J are prepared samples, respectively, AgPST, AgPCT, AgPCCT, AgPCaT (UV), and AgPCaT (vis).

Chapter 5 has been divided into two parts.

Part A investigates the synthesis of silver nanoparticles on PEG-PU-TiO_2 polymer nanocomposite films, its characterization and application as an antibacterial substrate. PEG- PU-TiO_2 polymer-nanocomposite films were synthesized by solution casting technique and silver has been deposited into these films by photochemical reduction of silver nitrate solution under UV light. XRD and XPS confirmed the deposited silver to be in metallic state. EDAX showed the amount of deposited silver was 2 to 4 at %.

The antibacterial activity of the silver incorporated polymer-titania nanocomposite films were studied on *E. coli* and *B. subtilis* by the disk diffusion method. These films have shown excellent antibacterial activity, even better than standard antibiotics with the added advantage of repeated use. Further, these films

were active even when tested in the microbial broth. Uniqueness of these films is, they can be used repeatedly as antibacterial substrates by simply washing after each use.

Table 1. Catalytic performance of PPd(0) and the recovered PPd(0) in successive Suzuki coupling cycles.[(a)]

Entry [a]	Catalytic cycle	Conversion [%]
1	1	>99
2	2	>99
3	3	98
4	4	98
5	5	98
6	6	98
7	7	98
8	8	98
9	9	98

[a] Reaction condition: 1-Iodo-4-nitrobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), K_3PO_4 (1.25 mmol), catalyst PPd(0) 40 mg (Pd wt% 2.88).

Part B of this thesis describes the synthesis of metallic palladium in PEG-PU polymer networks. Pd^{2+} ions containing PEG-PU polymer network films were prepared by solution casting technique. The incorporated Pd^{2+} ions were reduced by sodium borohydride to obtain metallic palladium. The free standing films were characterized by FT-IR, XRD, NMR, AAS, XPS and UV-DRS. FT-IR and NMR showed the structure and composition of the films whereas; XRD, XPS and UV-DRS confirmed the metallic nature of palladium.

The palladium containing films find excellent application in catalysis. They are efficient and convenient catalyst systems for hydrogenation reaction of a number of unsaturated organic compounds. They even find application as a catalyst for

Suzuki cross-coupling reactions for substituted iodo- and bromoarenes. The catalyst film is easily recoverable from the reaction mixture just by cotton filtration. It can be recycled up to at least ten cycles for hydrogenation and Suzuki coupling reaction of iodoarenes. Furthermore, there is no indication of either palladium or polymer leaching during the reaction as evidenced by AAS and NMR analysis respectively.

The thesis ends with the final conclusions drawn from the work and scope for future research in this area.